INORGANIC POWDERS WITH SELECTIVITY TOWARDS CARBON MONOXIDE, HCN OR NO

FIELD OF THE INVENTION

A new filter containing a polymer network having a protein encapsulated in the polymer network. The protein is encapsulated within the polymer network and not just precipitated or supported on an active support. The protein is frozen in the polymer network. Chemical additives can also be present to stabilize the protein. The invention also relates to a device that can work as a color change indicator when carbon monoxide("CO") or NO is passed through the device. The invention relates to binding molecules, wherein the protein or other molecules, are responsible for the selective binding of gases. The other molecules preferably contain at least one inorganic element.

BACKGROUND OF THE INVENTION

The encapsulation of biologically active molecules in an inorganic matrix is providing a new base of materials that are finding ever-increasing applications, particularly in bio-sensing (see E.H. Lan, B.C. Dave, J.M. Fukuto, B. Dunn, J.I. Zink and J.S. Valentine, *J. Mater. Chem.*, 9 (1999) 45; J. Lin and C.W. Brown, *Trends in Analytical Chem.*, 16 (1997) 200 and M. Tess and J.A. Cox, *J. Pharmaceutical and Biomedical Analysis*, 19 (1999) 55). Synthetic strategies are employed to retain biological function of the encapsulated bio-molecule. Strategies reported include alkoxide-based sol-gel processing; see N. Shibayama and S. Saigo, *J. Mol. Biol.*, 251 (1995) 203; H.H. Weetall, *Biosensors & Bioelectronics*, 11 (1996) 327; J.M. Miller, B. Dunn, J.S. Valentine and J. I. Zink, *J. Non-crystalline solids*, 202 (1996) 279; C. Shen

and N.M. Kostic, *J. Electroanalytical Chem.*, 438 (1997) 61; L. Zheng, K. Flora and J.D. Brennan, *Chem. Mater.*, 10 (1998) 3974; T. Keeling-Tucker, M. Rakic, C. Spong and J.D. Brennan, *Chem. Mater.*, 12 (2000) 3695 and B. Dunn, J.M. Miller, B.C. Dave, J.S. Valentine and J.I. Zink, *Acta Mater.*, 46 (1998) 737 and aqueous sol-gel processing; R.B. Bhatia, C.J. Brinker, A.K. Gupta and A.K. Singh, *Chem. Mater.*, 12 (2000) 2434 and aqueous colloidal sol-gel processing; D.-M. Liu and I.-W. Chen, *Acta Mater.*, 47 (1999) 4535. In the bulk of these studies, aged (wet) silica gels were formed either as monoliths or thin films. Important demonstrations of stabilization and function retention of the encapsulated bio-molecule were made.

An alternative application for encapsulated bio-molecules is in the area of selective gas phase adsorption. The heme proteins, for example, hemoglobin, myoglobin, etc., are well known to bind oxygen, carbon monoxide and nitrous oxide. For this application, powders or ultra-thin coatings are required, in order to ensure a high gas flux through the adsorbent. Specific areas of concern for protein encapsulation include protein denaturation during processing. Proteins can denature during poly-condensation reactions occurring as the gel is forming. During thin film and powder formation, the shrinkage and collapse of the pore structure is an additional concern.

A freezing process for the formation of silica powders is disclosed in W. Mahler and U. Chowdhry, "Ultrastructure Processing of Ceramics, Glasses and Composites," edited by L. Hench and D. Ulrich, John Wiley and Sons, 1984.

US patents 3,693,327 (" '327 patent") and 3,982,987 disclose filters suitable for removing carbon monoxide from gasses passed through the filter. The filter can be used as a cigarette filter. The air filter medium in the '327 patent contains amorphous

hemoglobin, crystalline hemoglobin, amorphous heme or crystalline heme in stoichiometric excess.

US patent 4,612,333 discloses filter composition comprising a foamed gypsum material containing carbonaceous material dispersed throughout the foamed gypsum (col. 2, lines 4-48). The carbonaceous material can be an activated carbon, dried blood (hemoglobin) or comminuted vegetable matter (col. 2, lines 48-53). A polymer is used to make the foaming system (col. 2, lines 15-32).

SUMMARY OF THE INVENTION

A filter according to the present invention comprises a polymeric matrix having a protein encapsulated in said polymeric matrix. The filter is preferably a cigarette filter. The polymer matrix can be a polymeric powder or gel. It is preferably a gel such as organic or inorganic gel. The polymeric matrix would have an encapsulated active component incorporated in the matrix. A powder can be prepared by the incorporation of a protein into a polymeric gel such as silicic acid gel followed by a fast freezing and thawing that preserves the open polymeric network and the activity of the protein. The powder can be used as a selective filter.

This active powder could be used in cigarette filters for the removal of carbon monoxide from mainstream smoke. The active powder could be synthesized in a powder form or it could be gelled or precipitated in situ on a filter support or a fibrous support. The dry powder could be used as a color change indicator in the cigarette filters. The powder can be used in a clear filter section as an indicator of reaction with carbon

monoxide. It could also be used in a breakable vial or in other similar forms as means to detect the presence of carbon monoxide.

Filters prepared in this manner would be important in other applications in other areas where the removal of carbon monoxide is desirable or necessary. It can be used in the automotive industry.

An object of the invention is to synthesize an adsorbent material with selectivity towards carbon monoxide (CO), nitric oxide (NO) and/or cyanide (CN).

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 illustrates UV/Vis spectra of the polymeric gels according to the invention.

Figure 2 illustrates the color differences between a) pure SiO_2 powder, b) 83 μM Mb/SiO_2, c) 50 μM Mb/SiO_2 and d) 27 μM Mb/SiO_2.

Figure 3a illustrates the UV/Vis spectra of oxy and deoxy-myoglobin/SiO_2

Figure 3b illustrates the visual bands of deoxy-myoglobin and CO bound deoxy-myoglobin

Figure 4 illustrates the stabilization of the Fe2+ state in Mb (myoglobin) with the addition of cysteine.

Figure 5 illustrates the stabilization of the Fe2+ state in Hb (hemoglobin) with the addition of cysteine.

Figure 6 illustrates the potential of binding CO in Hb encapsulated powders containing cysteine.

Figure 7 illustrates the color difference between deoxy-Mb and CO bound Mb.

Figure 8 illustrates the kinetics of CN^- binding to metHb.

Figure 9 illustrates the kinetics of CO binding to Hb (deoxy).

Figure 10 illustrates the relative reductions in the 4th puff for gas phase main stream smoke components.

Figure 11 illustrates the relative reductions for the total of 8 puffs for gas phase main stream smoke components.

Figure 12 illustrates a UV/visible spectra showing cyanide interaction with hemin-Cl / pyridine entrapped in silicic acid powder.

Figure 13 illustrates a UV/visible spectra showing cyanide interaction with cobalt tetraphenylporphyrin / pyridine entrapped in silicic acid powder

Figure 14 illustrates UV/visible spectra showing cyanide interaction with cobalt tetraphenylporphyrin / pyridine entrapped in TEOS powder according to the invention.

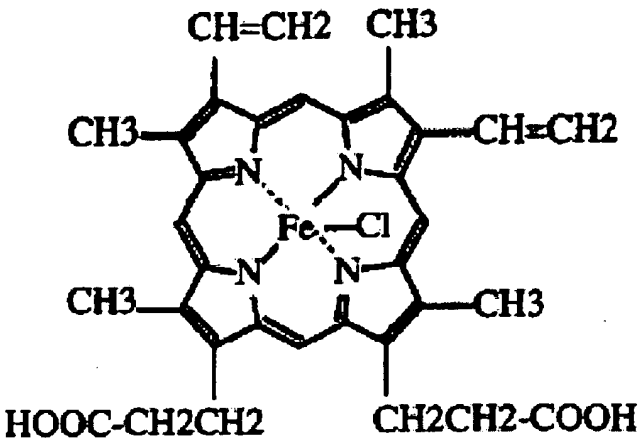
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A filter which comprises a polymeric matrix having a protein encapsulated in said polymeric matrix. The protein or other binding molecules are preferably encapsulated in an inorganic or organic polymeric structure such as, but not limited to structures originating from a polymeric gel. The polymeric gel leads to the high surface area of the final powder.

The proteins or other binding molecules can be, but are not limited to heme proteins, for example, hemoglobin, myoglobin, simple porphyrins or complex

chemically modified porphyrins with extra functionalities, beta vitamin or chlorophyll etc. These proteins and other binding molecules can bind oxygen, carbon monoxide and nitrous oxide.

Heme has the following formula:



When Fe is in the 3^+ state, it binds CN-, NO, OH^-, H_2O and pyridine.

When Fe is in the 2^+ state, it binds O_2, CO, NO and pyridine.

Auto-oxidation occurs in hemes when the pH is low and the O_2 content is high. Auto-oxidation is promoted with an Fe(III) ligand and water. It is preferable to create an environment where auto-oxidation is limited. This can occur by minimizing the amount of H_2O or the dimerization. There are several possible ways to limit the auto-oxidation, one such way is by sorption of the heme into a mesoporous material. Another way to limit the auto-oxidation is to anchor the heme onto a silica surface such as, but not limited to covalent grafting. A further way to limit the auto-oxidation is by encapsulating the heme with a functionalized silica gel.

The inorganic polymers are preferably those of a silica (SiO_2) matrix.

Examples of organic polymers include, but are not limited to: polyacrylic acid, carboxymethylcellulose and other cellulose derivatives, chitosan, gelatin, carageenan, pullulan, alginates, etc. and their modified analogs or copolymers as crosslinked or uncrosslinked systems. The polymers are preferably not foaming polymer such as the polymeric foams described in US 4,612,333.

The freezing technique used to produce the silica matrix can also be used to produce zirconia gels as described in W. Mahler and U. Chowdhry, "Ultrastructure Processing of Ceramics, Glasses and Composites," edited by L. Hench and D. Ulrich, John Wiley and Sons, 1984 ("Mahler"). Silica gels described in Mahler can be prepared from silicic acid. The acid is synthesized by passing a dilute sodium silicate solution containing approximately 6.0 weight percent SiO_2 through an ion exchange column packed with a strong cation exchange resin, for example, Rexyn 101M, R 231 (from Fischer Scientific) The process exhanges sodium ions for protons, and the effluent from the column is a cear solution of sdium free silicic acid, pH of about 3 containing the 6% by weight SiO_2.

In freshly prepared silicic acid solutions, the silicic acid has a number average molecular weight of about 500 to 1500. As the polysilicic acid ages, the molecular weight increases. With further aging, the solution gels and the molecular weight continues to increase.

A gel can be obtained by adjusting the pH of the silicic acid to 5 with $1M$ NH_4OH and letting it age for 30 minutes. It was then frozen unidirectionally by placing in to a $-70^{\circ}C$ bath at a rate of 4 cm/hr. The frozen mass was then allowed to thaw at room

temperature. The product obtained was silica fibers having about 50 μm in diameter and 15 cm long.

Other organic polymer systems that may gel or precipitate out and form porous solids through either evaporation, freezing, pH changes, precipitation triggering agents may also be used to encapsulate the protein. Examples of these polymer candidates include, but are not limited to: polyacrylic acid, carboxymethylcellulose and other cellulose derivatives, chitosan, gelatin, carageenan, pullulan, alginates, etc. and their modified analogs or copolymers as crosslinked or uncrosslinked systems. Volatile additives can be added in the system to provide porosity upon evaporation of the volatile additive.

A powder can be made by freezing a polymeric gel at temperatures about 77 K. The cooling temperature can be higher than 77 K as long as the gel freezes (below the freezing point of the aqueous solution). Fast freezing leads to a homogeneous, high surface area powder. Then it is preferable to thaw the frozen polymeric gel. The thaw process can be done at room temperature (23°C) or at a slightly elevated temperature up to about 75°C. An alternative could be to draw vacuum on the frozen gel. This procedure could be done under different temperatures or temperature profiles depending on the polymer system and the target porosity. The thawed product can optionally be filtered and then optionally dried. An active powder is formed.

This active powder could be used in cigarette filters for the removal of carbon monoxide and NO from mainstream smoke. It could be synthesized in a powder form or it could be gelled or precipitated in situ on a filter support or a fibrous support. Again, preferably the form is an active powder or an ultra-thin coating. The powder or coating is

used to ensure a high gas flux through the adsorbent. Filters prepared in this manner would be important in other applications in other areas where the removal of carbon monoxide is desirable or necessary. The powder could also be combined with a binder and formed into larger granular particles or even extruded in different shapes as may be required by the application (larger particles may be used to address pressure drop limitations).

The filters of this invention also work without the use of a foamed gypsum.

Examples

One method of preparing a polymer encapsulated protein powder is described below. SiO_2 encapsulated myoglobin powder is made as follows. The protein used was horse heart myoglobin. The protein was incorporated into the SiO_2 matrix in a non-destructive fashion thereby retaining its biological activity. The preparation of such powders involved incorporation of the protein into a silicic acid gel followed by a fast freezing technique that preserves the open polymeric gel network in powder form. UV/Vis spectroscopy was used to verify that the myoglobin remained intact in both the gel and powder forms.

Silica gels were produced by cation exchange of a 6% wt. sodium silicate solution. The resulting silicic acid solution was adjusted from an acidic pH preferably from about 2.5 to about 6 in order to induce gellation. Gels containing 83, 50 and 27 μM myoglobin (Mb) were made by adding the appropriate amount of 200μM Mb solution to the silicic acid solutions immediately following the pH adjustment. The gels were stirred for 5 minutes then allowed to age undisturbed for 18 hours at room temperature. UV/Vis spectra of the resulting aged gels are presented in Figure 1. The bands located at 500 and

630 nm are the bands corresponding to oxymyoglobin from horse heart. The shoulder on the 500 nm band and the band at 570 nm corresponds to the small amount of deoxy-myoglobin present in the starting myoglobin powder. The spectra compare directly with established literature values. See E. Antonini and M. Brunori, "Hemoglobin and Myoglobin in Their Reactions with Ligands," Elsevier Science, New York USA 1971.

After ageing, the gels were immersed rapidly in a liquid nitrogen bath. The fast freezing technique has been found to produce SiO_2 powders with surface areas as high as 1,000 m^2/g . During the freezing process, the polymeric gel network was trapped in intercrystalline gaps of ice. The freezing technique was believed to preserve the open polymeric structure of the gel leading to the high surface area of the final powder. This freezing technique is described in W. Mahler and U. Chowdhry, in "Ultrastructure Processing of Ceramics, Glasses and Composites," edited by L. Hench and D. Ulrich, John Wiley and Sons, 1984, in particular pages 207-217, which is incorporated by reference in its entirety for all useful purposes.

After warming to room temperature, the gels separated into a water phase and a wet gel phase. The water phase was removed by filtration and the wet gel was dried resulting in a SiO_2 powder. The gels made from 6% wt. sodium silicate solutions produce SiO_2 powders with a surface area of approximately 750 m^2/g with an average pore diameter of 8Å determined by 5 point BET surface area measurements.

After thawing the frozen SiO_2/Mb gels, the SiO_2 encapsulated myoglobin gels were filtered and then dried at ambient conditions in a class 1,000 laminar flow cabinet.

Figure 2 illustrates the color differences between a) pure SiO_2 powder, b) 83 μM Mb/SiO_2, c) 50 μM Mb/SiO_2 and d) 27 μM Mb/SiO_2. The brown color in the Mb loaded

powders was indicative of the presence of oxy-myoglobin. The BET surface areas of Mb series were 10, 60 and 220 m^2/g, respectively. The surface area of the Mb loaded powders was drastically reduced indicating successful encapsulation and elimination of the micropores found in the pure SiO_2 powders. Removal of the Mb by heating at 500°C for 3 hours results in white SiO_2 powders with BET surface areas around 550m^2/g.

In order to determine if the myoglobin had been incorporated into the SiO_2 powder without damaging the biological activity of the protein, 100 mg of 83 μM Mb/SiO_2 was loaded in a cuvette with a small amount of pH 7.4 phosphate buffer. The particles were then suspended in glycerin to prevent settling. The UV/Vis spectrum of oxy-myoglobin was recorded from 350 to 700 nm. The oxy-myoglobin/SiO_2 was reduced to deoxy-myoglobin/SiO_2 by adding a small amount of sodium disulfite to the cuvette. Figure 3a presents the UV/Vis spectra of oxy and deoxy-myoglobin/SiO_2. The shifting in the Soret band of horse heart myoglobin from 410 nm to 430 nm was the classic indication of the shift from oxy to deoxy-myoglobin (see E. Antonini and M. Brunori, "Hemoglobin and Myoglobin in Their Reactions with Ligands," Elsevier Science, New York USA 1971).

Shifts in the Soret band were negligible when CO was bound to deoxy-myoglobin. A much greater amount of shifting was realized in the visual bands. In order to detect the visual bands, 250 mg of 83 μM deoxy-Mb/SiO_2 was added to a cuvette and suspended in glycerin. The spectrum was recorded from 520-590 nm. In order to introduce CO, the cuvette was covered and a small amount of CO was injected by syringe. After a brief mixing period, the suspended particles became a bright red. Figure 3b illustrates the visual bands of deoxy-myoglobin and CO bound deoxy-myoglobin.

The band located around 530 nm evidenced the spectrum of the deoxy-myoglobin/SiO2. The broadening and small shoulder on the 530 nm band was attributed to a trace amount of unreduced oxy-myoglobin. When CO was bound to the myoglobin, the 530 nm band splits into two bands at 540 and 570 nm both exhibiting higher absorbance of light. This shifting and splitting is illustrated in the spectrum labeled CO-bound deoxy-Mb/SiO_2 in Figure 3b.

In another example, L-cysteine was added in a 2:1 molar ratio to heme groups (four in hemoglobin, one in myoglobin). The L-cysteine stabilized the oxyhemoglobin (CO-active) over methemoglobin (CO-inactive).

In the following examples, several SiO2 powders were tested for their removal potential of main stream smoke components. The cigarettes were prepared by creating a cavity containing 50 mg of powder in between cellulose acetate ("CA") plugs in the filter. To create the cavity, the CA plug was removed from the filter tube of a control cigarette. A section of the CA filter was then cut and reinserted in the filter tube. Following, fifty mg of powder were loaded in the filter. The remaining section of the originally removed CA plug was then reinserted in the filter tube to complete the CA/Silica/CA filter configuration. The control cigarette was an industry standard 1R4F cigarette. The gas phase components of the main stream smoke were analyzed using GC-Mass Spectroscopy, while the cigarettes were smoked at FTC conditions (2 second 35 cc puff with one puff taken every minute).

Table I

Cigarette	1,3-butadiene	1,2-propadiene	1,3-cyclohexadiene	hexane	benzene	toluene	acrolein	Methyl propyl ketone	HCN	acrylonitrile
Control- No Silica	101	98	100	102	102	105	103	101	99	107
Silica-Mb (1)	81	75	64	100	69	56	39	34	45	49
Silica-HSA(2)*	98	102	89	102	84	83	70	58	77	82
Silica-LSA (3)*	102	91	89	95	89	85	71	51	105	89
MCM-APS (4)*	105	109	78	93	79	67	57	48	39	75
Silica-CH3 (5)*	96	101	84	99	84	83	63	37	77	60

*HAS=High Surface Area, LSA=Low Surface Area, MCM-APS=Amino Propyl Silane modified MCM silica, -CH3=methylated silica

Table II

Cigarette	1,3-butadiene	1,2-propadiene	1,3-cyclohexadiene	benzene	toluene	formaldehyde	acrolein	ketene	HCN
Control- No Silica	99	100	94	102	105	104	118	106	104
Commercial Silica-HAS*	90	102	75	89	86	42	29	96	88
Silica-Mb (1)	80	73	63	78	83	30	71	34	80
Silica-HSA (2)*	86	76	69	81	93	48	75	55	91
Silica-LSA (3)*	98	101	85	95	96	56	76	82	100
MCM-APS (4)*	91	92	71	83	91	42	50	89	87
Silica-CH3 (5)*	91	93	64	81	86	36	47	31	51

*HAS=High Surface Area, LSA=Low Surface Area, MCM-APS=Amino Propyl Silane modified MCM silica, -CH3=methylated silica

Tables I and II show the results for several gas phase components. Table I contains results from the GC-MS analysis of the 4th puff, while Table II contains data from the total of eight puffs per cigarette. The same data are also shown in graphical form in

Figure 11. It is known, that porous adsorbents, and silica is one of them, will adsorb gas phase components and that the extent of removal is greater the greater the surface area of the adsorbent. Considering the surface area of silica containing myoglobin is reduced as myoglobin is encapsulated within the silica matrix, the above results demonstrate that myoglobin and specifically its protein component remove gas phase components such as dienes, aromatics, aldehydes, etc. at a greater selectively than unmodified silicas. The powders tested in this example were prepared more than three months prior to testing and were used in cigarette testing without any special preconditioning or treatment. The selectivity of the protein towards aldehydes is similar to the selectivity of the amino-propyl silane modified silica, which is another indication that certain compounds of the smoke stream are selectively chemisorbed onto the myoglobin impregnated silica.

Another method of incorporating the protein into the gel is as follows:

The molecule such as the hemin can be dissolved in a basic solution. The base promotes solvation of heme. Pyridine is a good base to use since it also minimizes dimerization. Then mix the hemin solution with silica solution prior to complete gelling. This also produces a good gel. The gel is a methyl-terminated silica gel. The trapped hemin within these gels is functionally intact. The hemin contains Fe(III) and binds HCN.

TESTING WITH GAS CONTAINING HCN

Powders suitable for gas absorption measurements were prepared and characterized by UV/visible spectrophotometry. The spectra of powders were done utilizing a 45° reflectance probe attached by fiber optic cable to a portable spectrometer

(Ocean Optics). This arrangement yields spectra which are far superior to those obtained on powders in the past utilizing other methods. This system exposes powders to known levels of high purity nitric oxide in a nitrogen gas stream to assess binding characteristics.

Several spectral characterization of powders were made using silicic acid as follows: A solution of 15 grams of sodium silicate in 150 ml. of water is prepared. This solution is passed through a column loaded with Rexyn (from Fischer Scientific). This column treatment changes the pH of the solution from pH 11 (initial solution) to pH 3 (column eluent). All eluent fractions below pH 3.5 are collected and pooled. Raising the pH of this solution causes solidification.

The following data collected on fiber-optic reflectance spectroscopy system is illustrated in Figures 12-14.

Figure 12 illustrates the visible spectra of hemin-pyridine encapsulated using silicic acid. The spectra illustrates the powder before and after addition of cyanide. It can be seen that the peak at 616nm has been significantly shifted to the 642 nm. The change occurred within 2-5 minutes. The color of the powder was changed from a brown-green color to a brown-red color. Another words, powders with cyanide appeared reddish-brown in color while powders without cyanide have a greenish color. Observation of the Soret absorption bands (400- 450 nm) is not possible in these powders.

A similar experiment has been done for cobalt-tetraphenylporphyrin-pyridine encapsulated using silicic acid (Figure 13). The figures shows a significant spectral shift of the Soret band from 432nm to 419 nm. However, this change was not rapid and occurred overnight. The color change was from a yellow color to a very pale yellow,

almost white color. The Soret absorption bands (400-450 nm) are well resolved in these powders.

These results suggest that the hemin and cobalt encapsulated in the gel are accessible and unhindered and capable of binding.

Figure 14 shows the spectral results of binding CN gas to the cobalt-tetraphenylporphyrin-pyridine encapsulated using TEOS. There was no significant color change observed. The Soret peak was shifted slightly from the 430nm to the 432nm and a new peak at 537 nm appeared.

The changes observed from CN binding to cobalt-tetraphenylporphyrin-pyridine in silicic acid and TEOS are significantly different. In the case of silicic, the Soret band is shifted to the higher energy level (blue shift), while in the case of TEOS, there is a slight shift a lower energy level. The differences might be attributed to the environment provided by the encapsulating material.

The device according to this invention can be used in other applications besides filters where the detection of carbon monoxide, HCN and/or NO is desirable or necessary. The device can be used as a CO, HCN and/or NO detector. The device would contain the dry powder encapsulated with active components as described above used in the filter. To detect the desired gas (CO,HCN or NO) the device would contain a clear or transparent section that contains the dry encapsulated powder. This section is preferably transparent, although, translucent would also work. Transparent is defined permitting the complete passage of rays of visible light through. Translucent is defined as permitting the partial passage of rays of visible light. When gas is passed through the device, the powder changes upon reaction with the carbon monoxide gas. Potentially the

strength of color change could be used to semi-quantitatively measure carbon monoxide present in the air or other fluid streams. If the section does not change colors than there is no gas (CO,HCN and/or NO) present in the air, gas or fluid stream that was passed through the device.

While this invention has been described with respect to particular embodiments thereof, it is apparent the numerous other forms and modifications of this invention will be obvious to those skill the area. The appended claims and this invention generally should be construed to cover all such obvious forms and modifications, which are within the true spirit and scope of the present inventions.

All the references discussed above are incorporated by reference in their entirety for all useful purposes.

WHAT IS CLAIMED IS

1. A cigarette filter which comprises a polymeric matrix having a protein or a molecule containing an inorganic element or a mixture thereof wherein said protein , said molecule or said mixture thereof is encapsulated in said polymeric matrix.
2. A filter which comprises a polymeric matrix having a protein, a molecule containing an inorganic element or mixture thereof, encapsulated in said polymeric matrix made by freezing a protein and a polymeric substance together and then thawing said protein and polymeric substance.
3. The filter as claimed in claim 2, wherein said polymeric matrix is an inorganic polymeric matrix.
4. The filter as claimed in claim 3, wherein said inorganic polymeric matrix is a silicon polymeric matrix.
5. The filter as claimed in claim 2, wherein said polymeric matrix is an organic polymeric matrix.
6. The filter as claimed in claim 2, wherein said molecule is a metalloporphyrin.
7. The filter as claimed in claim 2, wherein said protein is a hemoglobin or myoglobin.
8. The filter as claimed in claim 2, wherein the filter is a cigarette filter.
9. A process to make a filter, which comprises incorporating at least one protein or a molecule containing an inorganic element in a polymeric substance, freezing said protein or said molecule and polymeric substance to form a frozen mixture hen

thawing said frozen mixture to form an activated powder, and using the activated powder as a filter.

10. The process as claimed in claim 9, wherein said polymeric substance is a silicic acid gel.

11. The process as claimed in claim 9, wherein said polymeric matrix is an inorganic polymeric matrix.

12. The process as claimed in claim 9, wherein said polymeric matrix is an organic polymeric matrix.

13. The process as claimed in claim 9, wherein said molecule is a metalloporphyrin.

14. The process as claimed in claim 9, wherein said protein is a hemoglobin or myoglobin.

15. The process as claimed in claim 9, wherein the filter is a cigarette filter.

16. The process as claimed in claim 9, wherein the freezing occurs at temperatures less than about $-25^{\circ}C$.

17. The process as claimed in claim 9, wherein the freezing occurs at temperatures less than about $-50^{\circ}C$.

18. The process as claimed in claim 9, wherein the freezing occurs at temperatures of about $-70^{\circ}C$.

19. The process as claimed in claim 9, wherein the thawing occurs at about $23^{\circ}C$ or an elevated temperature.

20. A process to remove aldehyde and/or NO from smoke which comprises passing smoke through the filter as claimed in claim 2.

21. A process of detecting at least one gas selected from the group consisting of carbon monoxide, NO and HCN which comprises passing a gas containing carbon monoxide, NO or HCN or a mixture thereof through a filter comprising a polymeric matrix powder having a protein or molecule containing an inorganic element or mixture thereof encapsulated in said polymeric matrix and said powder changes colors when the carbon monoxide, NO or HCN passes through said filter.

22. The process as claimed in claim 20, wherein said filter is a transparent filter.

23. A device used for detecting carbon monoxide, NO or HCN which comprises a transparent or translucent section which contains a polymeric matrix powder having a protein or molecule containing an inorganic element encapsulated in said polymeric matrix and said powder changes colors when carbon monoxide, NO or HCN passes through said powder.

24. The device as claimed in claim 23, wherein said section is transparent.

25. A method for detecting the presence of CO, NO or HCN which comprises passing a gas or liquid through a device which comprises a dry powder encapsulated with active component, said powder changes colors upon reaction with said gas or liquid if said gas or liquid contains a carbon monoxide gas.

26. The method as claimed in claim 25, wherein said device has a transparent section and said powder is in said transparent section.

27. The method as claimed in claim 25, wherein said device has a translucent section and said powder is in said translucent section.

28. A process to make a filter, which comprises sorption of a protein in a mesoporous material thereby forming a filter material.

29. A process to make a filter, which comprises covalent grafting a protein onto a silica surface thereby forming a filter material.

ABSTRACT OF THE DISCLOSURE

A silica powder with encapsulated active components towards selective filtration is prepared by the incorporation of a protein or molecule containing an inorganic element into a polymeric substance followed by a fast freezing that preserves the open polymeric network and the activity of the protein or molecule containing an inorganic element. The encapsulated polymeric protein or molecule can be used as a color change indicator for CO, HCN or NO.

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Fig.1.

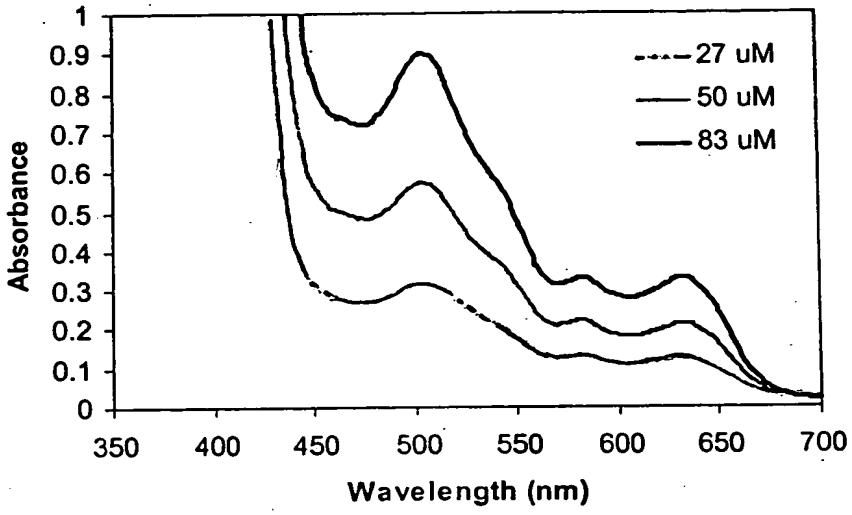

Absorbance
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
350
400
450
500
550
600
650
700
Wavelength (nm)
27 uM
50 uM
83 uM

Fig.2.

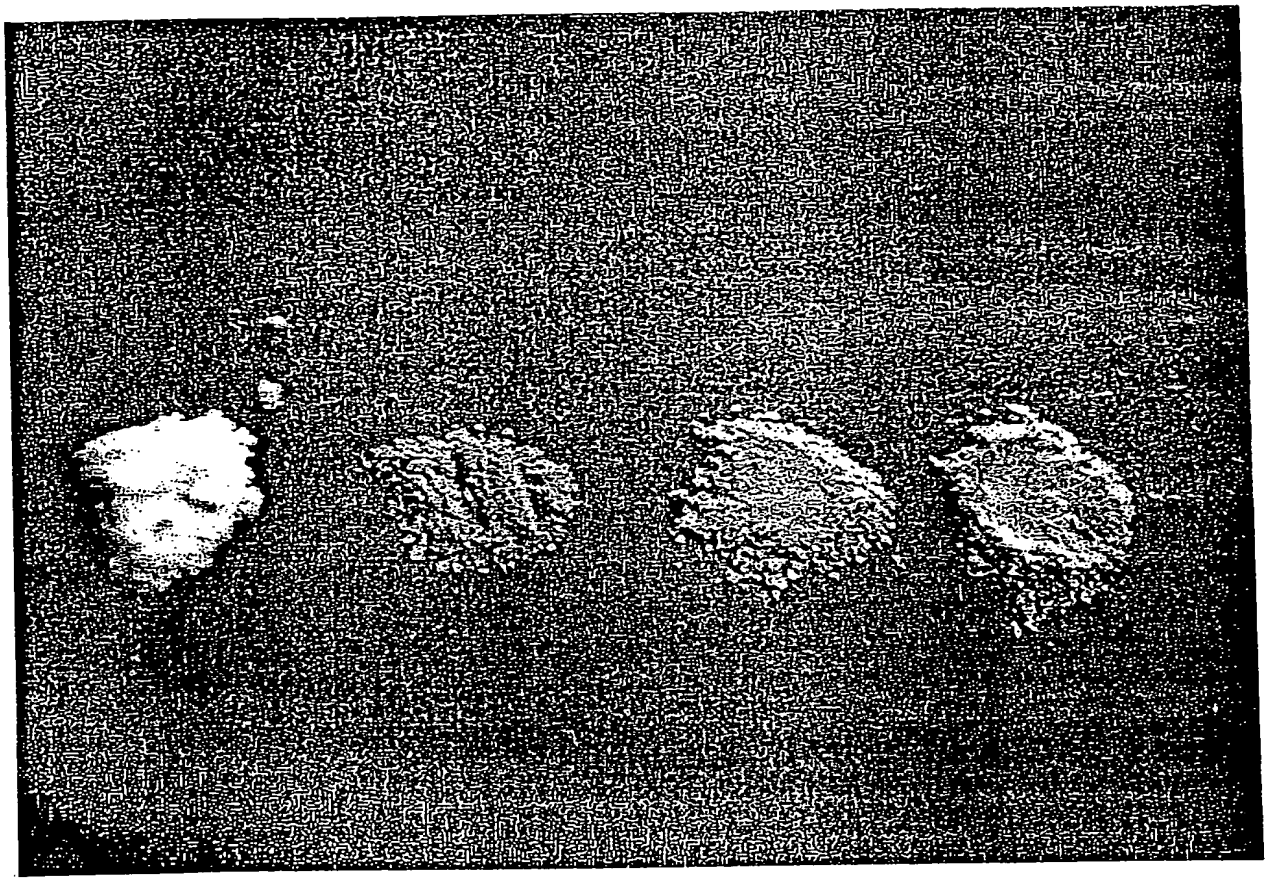
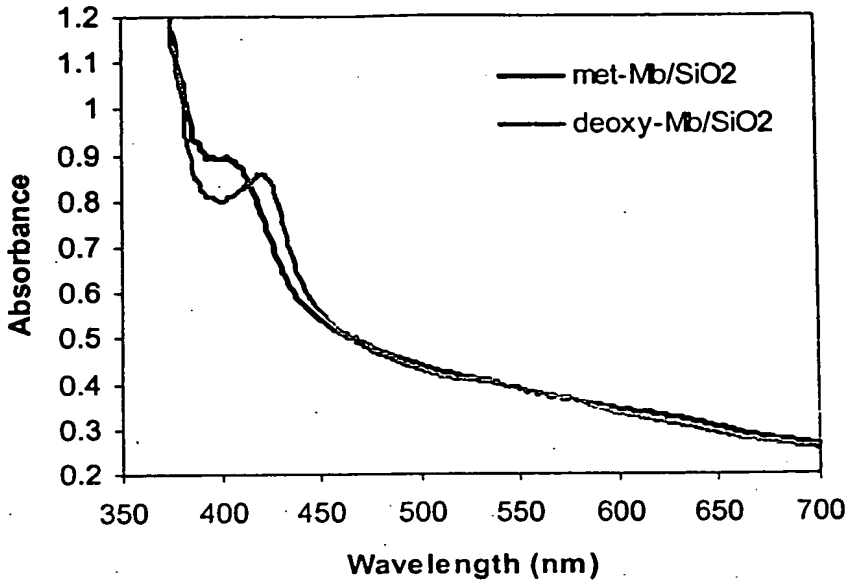


Fig. 3A.


1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
Absorbance
met-Mb/SiO2
deoxy-Mb/SiO2
350
400
450
500
550
600
650
700
Wavelength (nm)

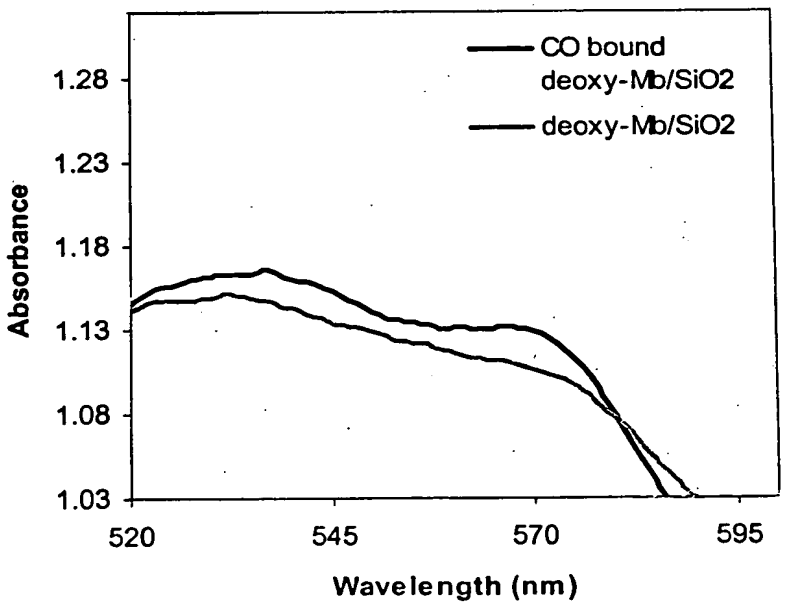

1.28
1.23
1.18
1.13
1.08
1.03
Absorbance
CO bound deoxy-Mb/SiO2
deoxy-Mb/SiO2
520
545
570
595
Wavelength (nm)

Fig. 3B.

Fig. 4.

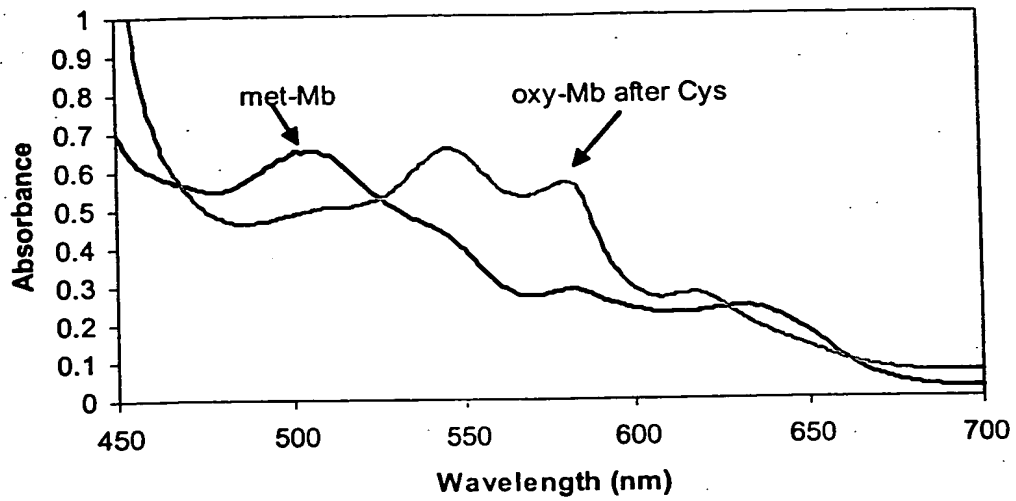
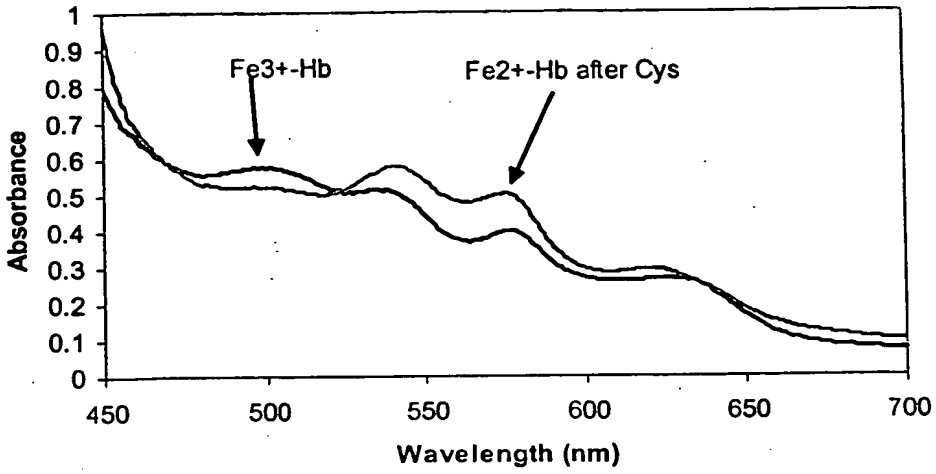

met-Mb
oxy-Mb after Cys
Absorbance
Wavelength (nm)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
450
500
550
600
650
700

Fig.5.


Fe3+-Hb
Fe2+-Hb after Cys
Absorbance
Wavelength (nm)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
450
500
550
600
650
700

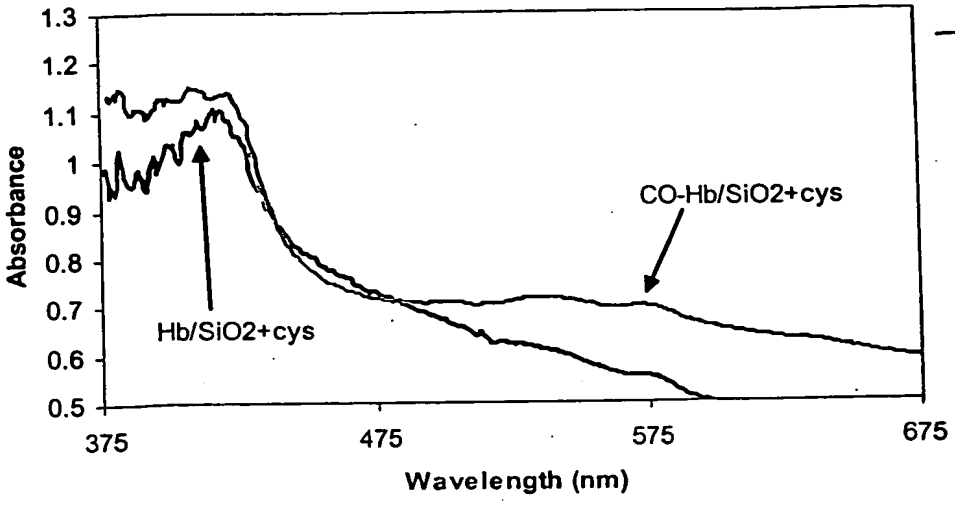

1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
Absorbance
CO-Hb/SiO2+cys
Hb/SiO2+cys
375
475
575
675
Wavelength (nm)

Fig.6A.

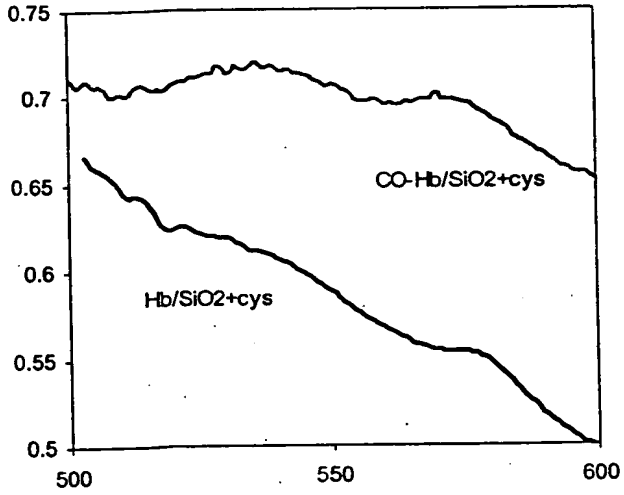

0.75
0.7
0.65
0.6
0.55
0.5
CO-Hb/SiO2+cys
Hb/SiO2+cys
500
550
600

Fig.6B.

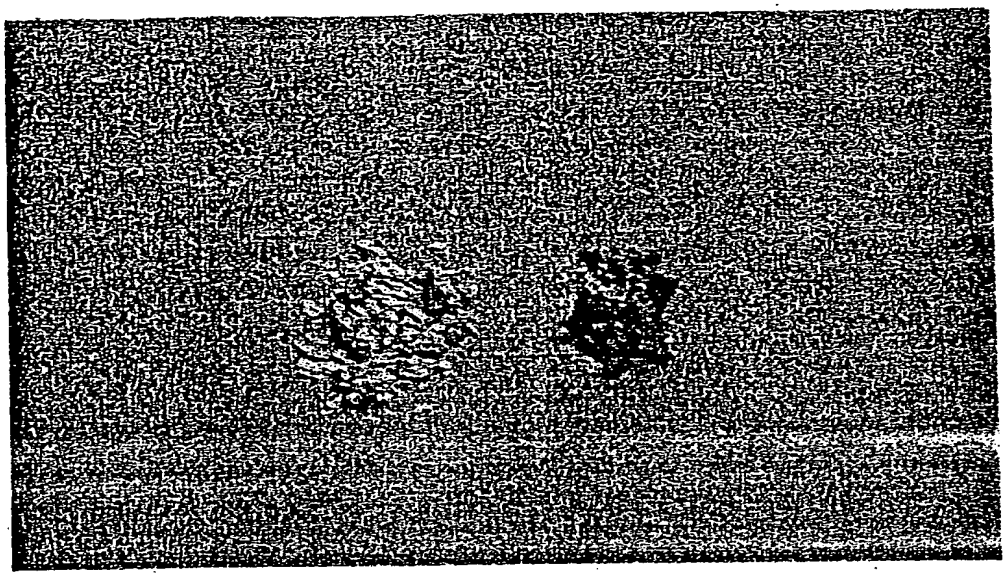


Fig. 7.

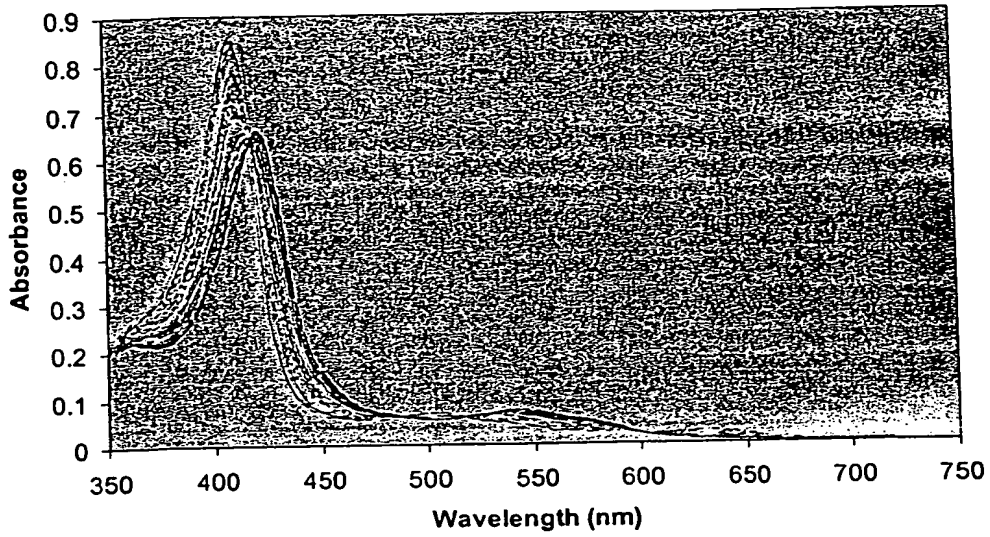

Absorbance
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
350
400
450
500
550
600
650
700
750
Wavelength (nm)

Fig.8A.

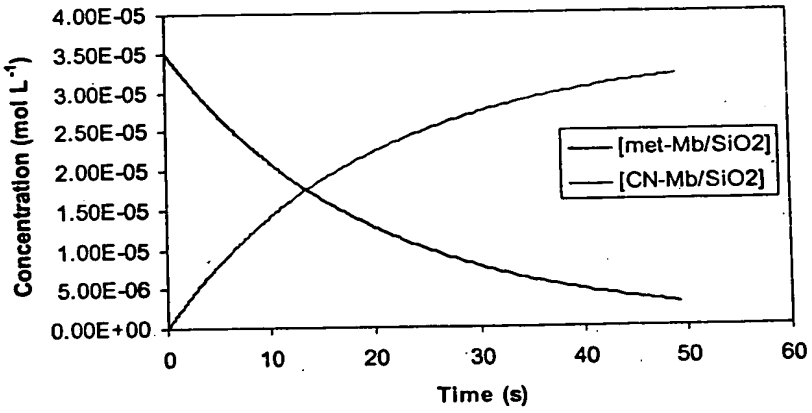

Concentration (mol L-1)
4.00E-05
3.50E-05
3.00E-05
2.50E-05
2.00E-05
1.50E-05
1.00E-05
5.00E-06
0.00E+00
0
10
20
30
40
50
60
Time (s)
[met-Mb/SiO2]
[CN-Mb/SiO2]

Fig.8B.

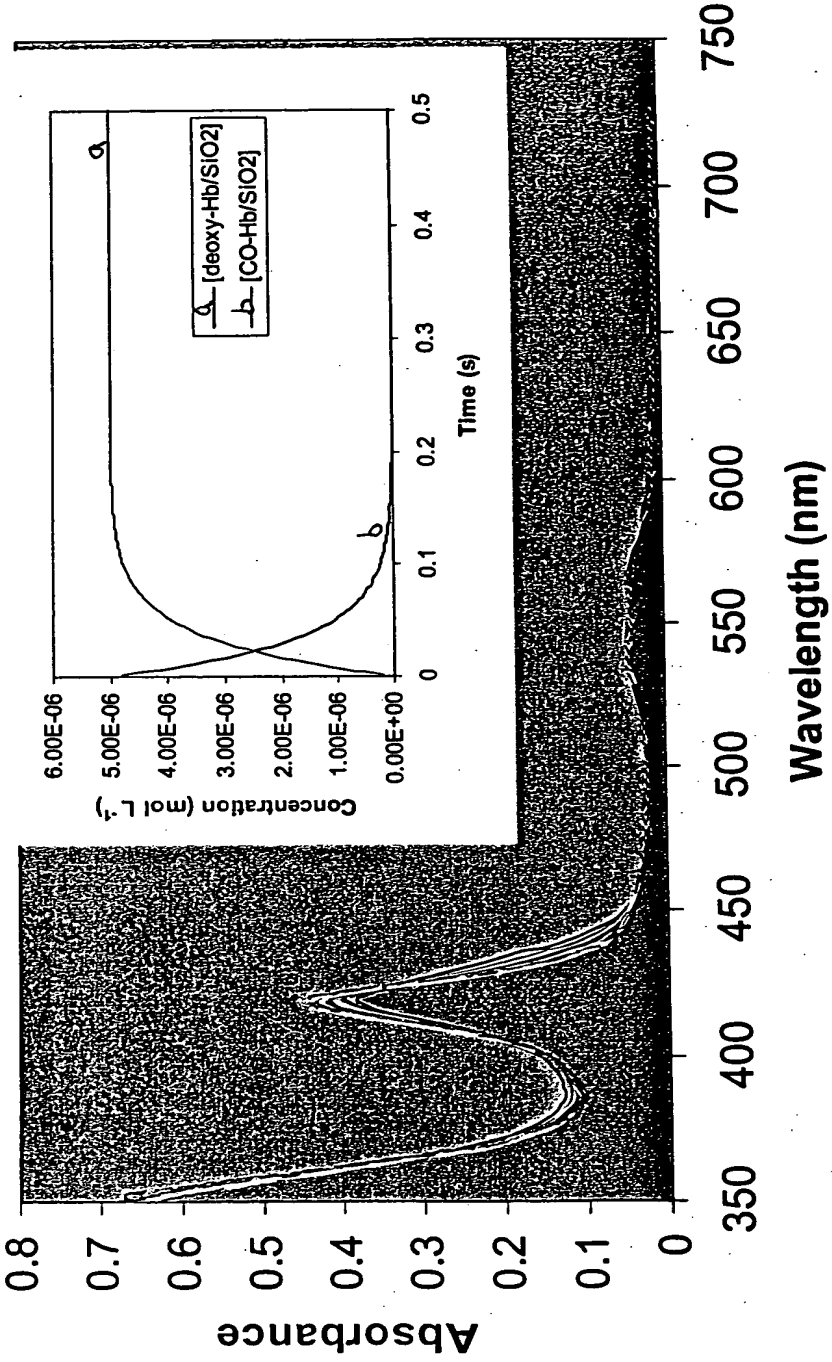

Absorbance
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
350
400
450
500
550
600
650
700
750
Wavelength (nm)
Concentration (mol L-1)
6.00E-06
5.00E-06
4.00E-06
3.00E-06
2.00E-06
1.00E-06
0.00E+00
0
0.1
0.2
0.3
0.4
0.5
Time (s)
a
b
[deoxy-Hb/SiO2]
[CO-Hb/SiO2]

Fig. 9.

Fig. 10.

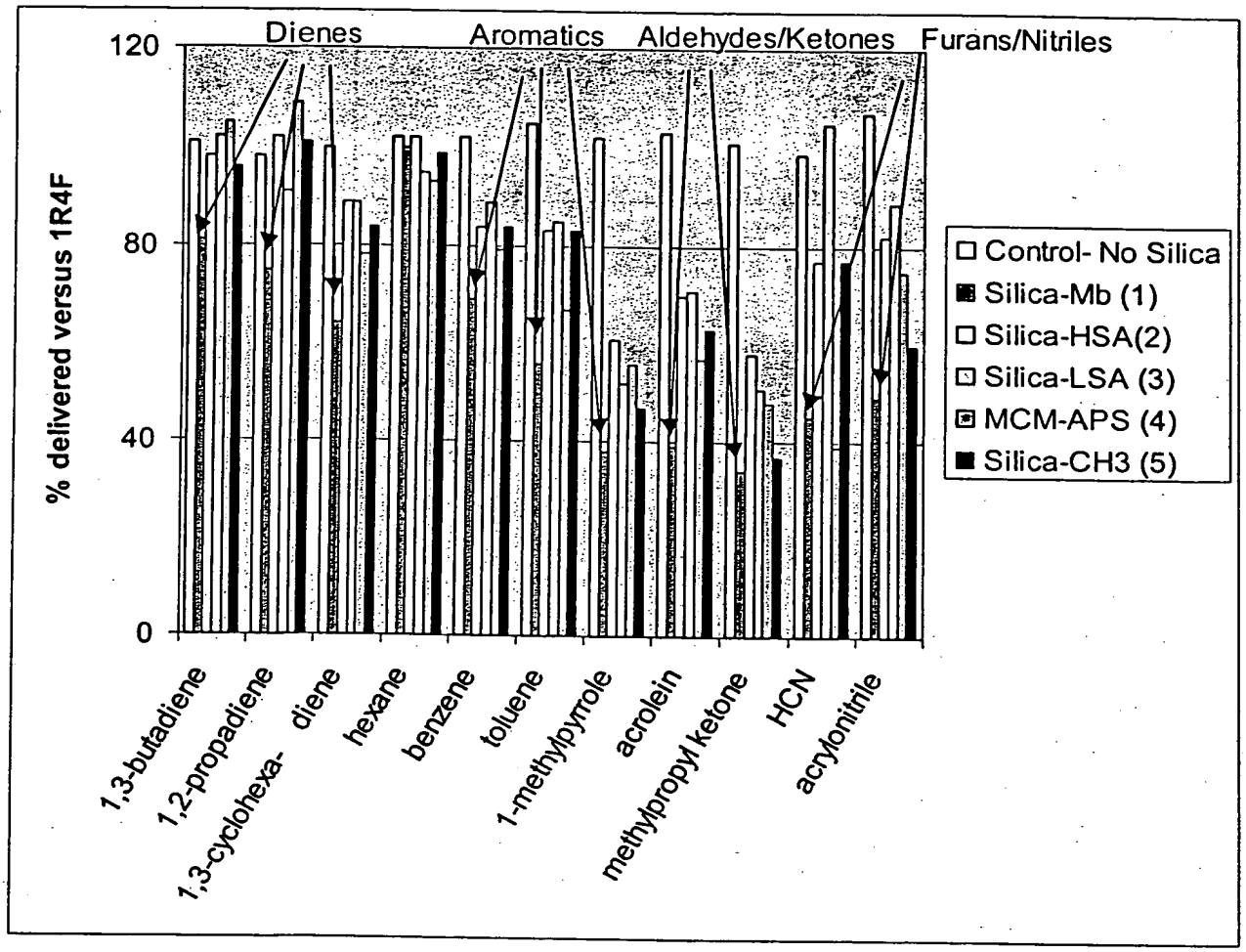

Dienes
Aromatics
Aldehydes/Ketones
Furans/Nitriles
% delivered versus 1R4F
120
80
40
0
Control- No Silica
Silica-Mb (1)
Silica-HSA(2)
Silica-LSA (3)
MCM-APS (4)
Silica-CH3 (5)
1,3-butadiene
1,2-propadiene
1,3-cyclohexa-diene
hexane
benzene
toluene
1-methylpyrrole
acrolein
methylpropyl ketone
HCN
acrylonitrile

Fig. 11.

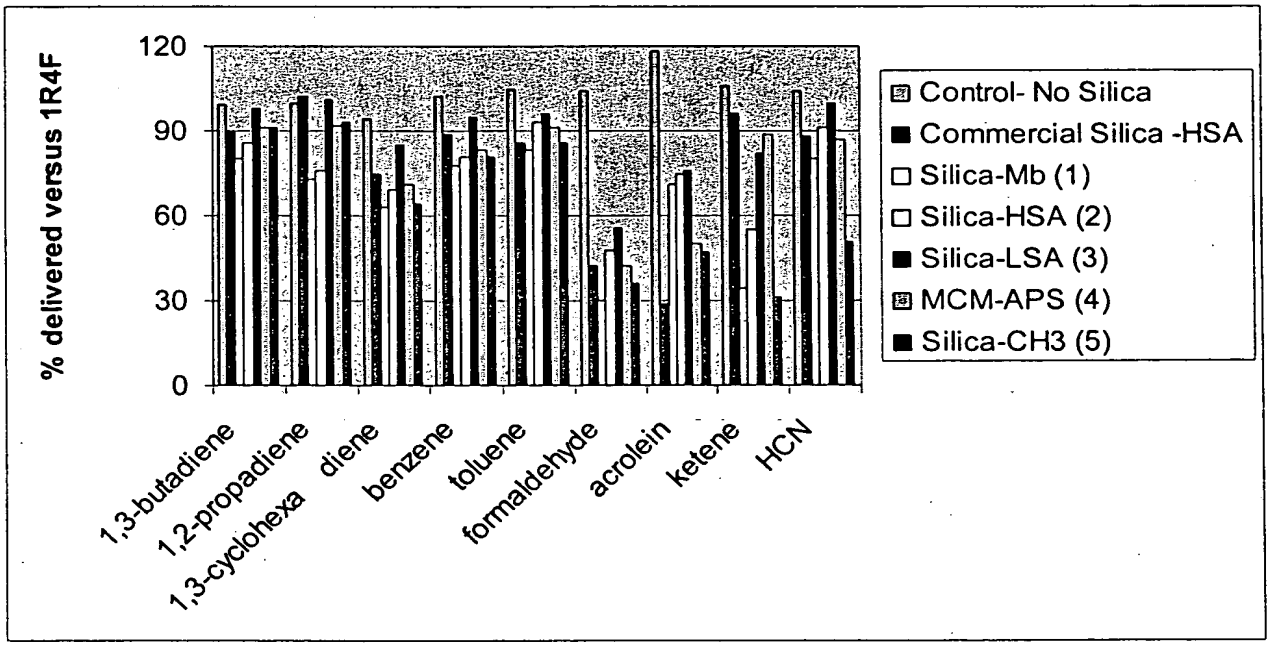

% delivered versus 1R4F
120
90
60
30
0
1,3-butadiene
1,2-propadiene
1,3-cyclohexa diene
benzene
toluene
formaldehyde
acrolein
ketene
HCN
Control- No Silica
Commercial Silica -HSA
Silica-Mb (1)
Silica-HSA (2)
Silica-LSA (3)
MCM-APS (4)
Silica-CH3 (5)

Fig. 12.

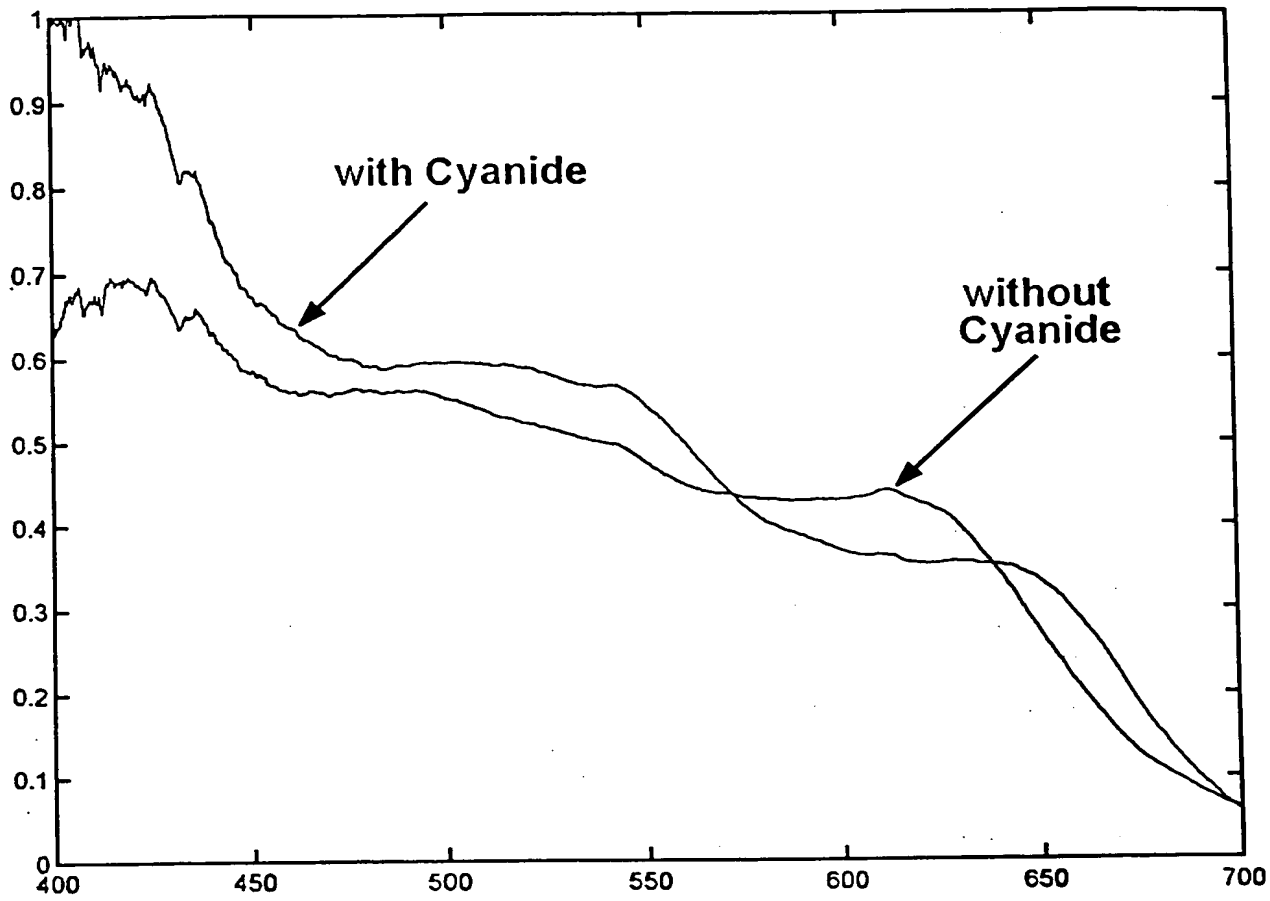

with Cyanide
without Cyanide
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
400
450
500
550
600
650
700

Fig. 13.

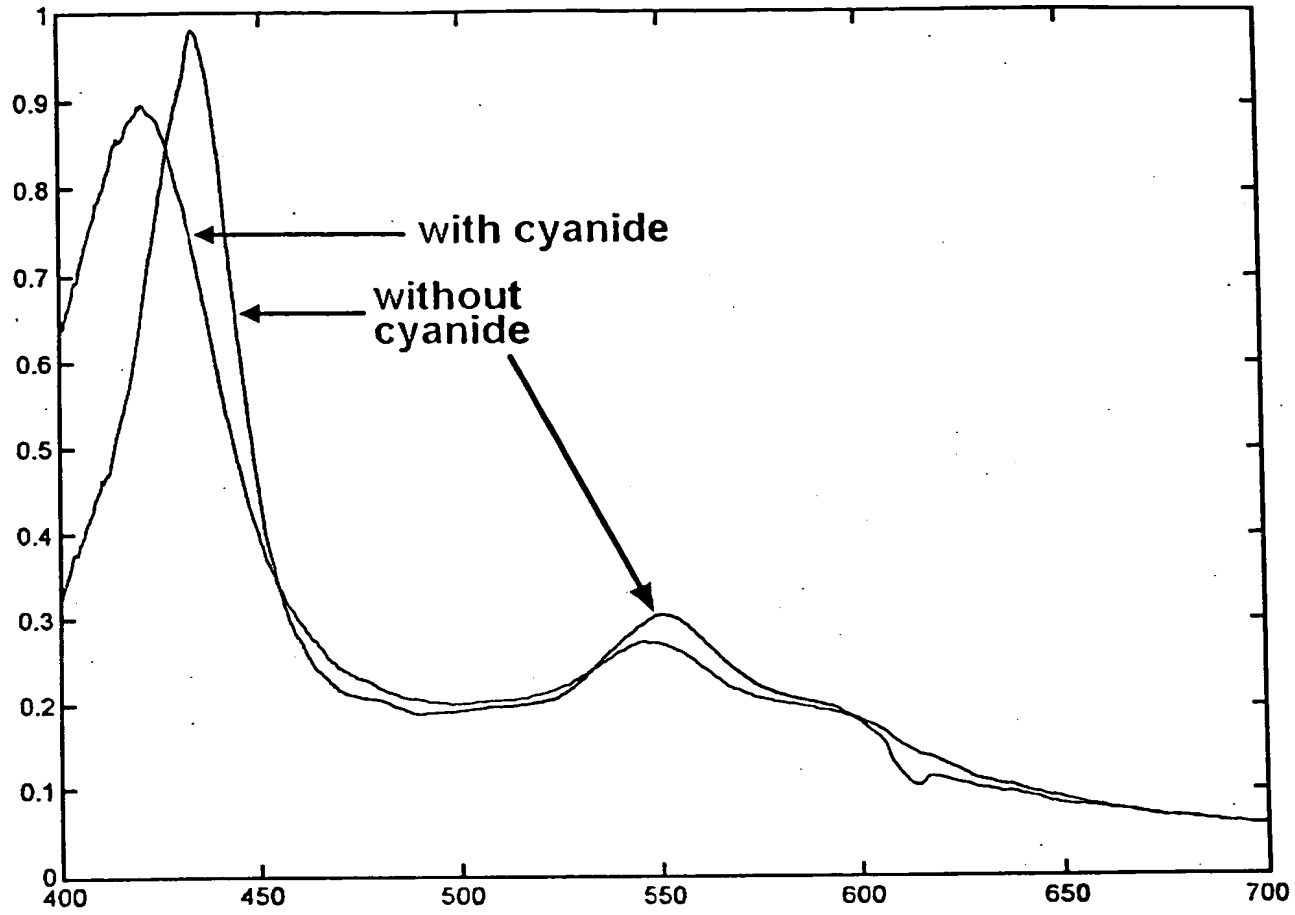
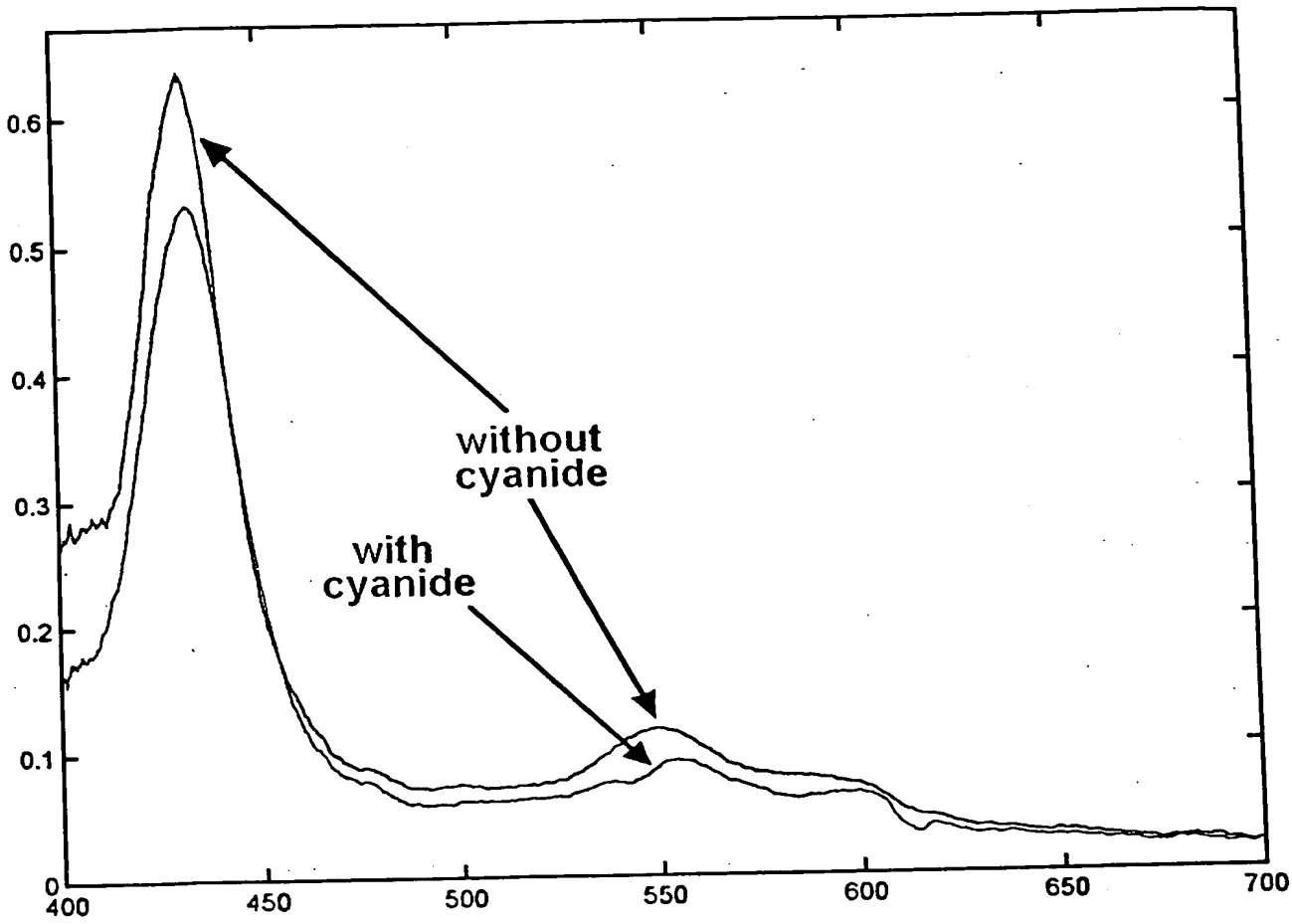

1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
400
450
500
550
600
650
700
with cyanide
without cyanide

Fig.14.


0.6
0.5
0.4
0.3
0.2
0.1
0
400
450
500
550
600
650
700
without cyanide
with cyanide